

# Resonant Auger studies of metallic systems

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(Received 1 October 1999; accepted 27 March 2000)

Results of resonant Auger spectroscopy experimental are presented for Cu, Co, and oxidized Al. Sublifetime narrowing of Auger spectra and generation of sublifetime narrowed absorption spectra constructed from Auger yield measurements were observed. Resonant Auger yields are used to identify three chemical states of oxidized Al. Partial absorption yield spectra were derived giving detailed electronic information and thickness information for the various chemical states of the bulk metal, the passivating aluminum oxide layer, and the metal-oxide interface region. In addition, the total absorption yield spectrum for the oxidized Al sample was constructed from the partial yield data, supporting the consistency of our method. © 2000 American Vacuum Society.  
[S0734-2101(00)12304-8]

## I. INTRODUCTION

Excitation energies far away from resonant conditions have been traditionally used to generate Auger electrons, where the Auger effect can be approximated by a two-step model which consists of the generation of a vacancy and its subsequent decay. Vacancy lifetimes play a key role in the inherent width of the spectral features observed when measurements are made far above absorption. Near an absorption edge, however, the process of excitation and decay are coupled leading to a double photoionization event that may be described in terms of an inelastic scattering model.<sup>1</sup> A wealth of interesting features near resonance results. So called spectator lines<sup>2</sup> of constant binding energy, due to excitation into bound states, may be observed at the absorption edge and are due to the same effect sometimes observed in radiationless resonant Raman scattering.<sup>2-4</sup> Furthermore, as the Auger linewidth is no longer limited by the intrinsic lifetime but rather by the lifetime of a new intermediate state. Sublifetime spectral widths may be observed given a sufficiently narrow excitation bandwidth.<sup>1</sup> Since Auger emission across a resonance reflects the density of unoccupied states that was probed by the selected transition,<sup>5</sup> absorption spectra may be measured using the Auger yield detection. Combined with sublifetime effects, the potential arises to determine the chemical and electronic nature of mixed valence systems. Work on resonant Auger spectroscopy has focused upon sublifetime narrowing issues,<sup>6-8</sup> spectator lines,<sup>9-11</sup> and other studies of the Auger process itself.<sup>12-14</sup>

Here, we report the results of soft x-ray experiments using

the resonant Auger effect. In addition to demonstrating traditional resonant Auger measurements, the ability to use resonant Auger signal as a probe to measure partial absorption yields from samples of mixed chemical states is demonstrated in this article.

## II. EXPERIMENT

The experiments were performed on the SRI-CAT 2-ID-C soft x-ray beam line at the Advanced Photon Source.<sup>15</sup> The beam line consists of a spherical grating monochromator with a series of gratings to provide an operational energy range of 0.5–3.0 keV and resolving powers up to 10 000. The beam size on the sample is approximately 0.5 mm in height by 2.0 mm in width. A flux of  $10^{12}$  photons/s reaches the sample at a resolving power of approximately 5000. The ultrahigh vacuum experimental chamber is equipped with a Physical Electronics 10-365A hemispherical energy analyzer with 16 channeltron detection and up to  $\sim 25$  meV resolution. The analyzer was mounted at  $53^\circ$  with respect to the incident photons in the horizontal plane. Auger yield measurements were recorded using the peak height as the photon energy was scanned across the resonance. Incident photon flux was monitored using a high-transmission gold mesh. Normal absorption measurements were recorded in total electron yield (TEY) mode by monitoring the charge compensation current and in total fluorescence yield (TFY) mode using a silicon photodiode. The Al, Cu, and Co samples were foils of minimum 99.99% purity acquired from Johnson Mathey. The Cu and Co were sputter cleaned prior to analysis using 1 keV and an Ar pressure of  $5 \times 10^{-5}$  Torr. The Al sample examined was left in an ambient oxidized condition.

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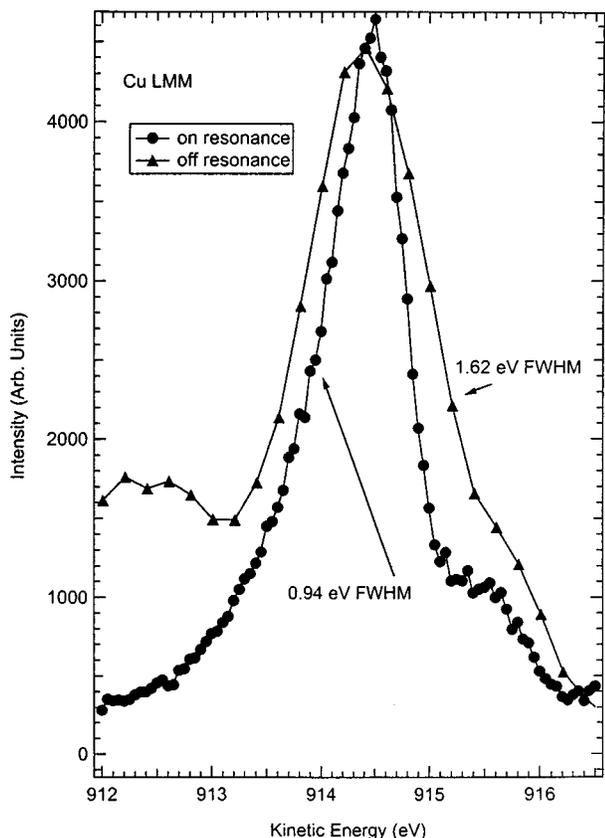


FIG. 1. Comparison of Cu  $L_3M_{4,5}M_{4,5}$  Auger spectra taken on, +0 eV, and off, +675 eV, resonance with respect to the Cu  $L_3$  edge.

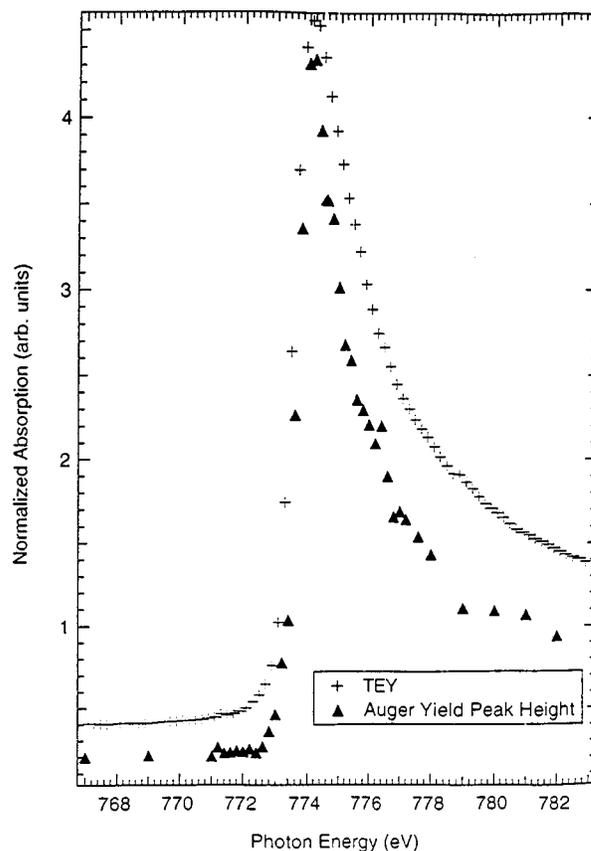


FIG. 2. Comparison of Co  $L_3$  edges measured by TEY and resonant Auger yield methods.

**III. RESULTS AND DISCUSSION**

Resonant sublifetime narrowing effects are clearly visible in the Cu  $LMM$  Auger spectra shown in Fig. 1. One spectrum was acquired at the Cu  $L_3$  edge, the other at a photon energy 675 eV above the edge. All other conditions with respect to the beam line and hemispherical analyzer resolution were kept the same. A significant decrease is observed in the width of the Auger peak off resonance, 1.62 eV, to on resonance, 0.94 eV. Narrowing is also observed in absorption spectra using Auger emission as a probe of the transition. Figure 2 shows the absorption spectra from clean Co. The Auger yield measurement was narrower than the TEY spectrum. Spectral features that are unresolvable due to the lifetime effects in off resonance may be resolvable in the resonance regime.

For many materials, the kinetic energy of Auger electrons are sensitive to their chemical state. Auger shifts are often larger than photoemission core level shifts on the same sample.<sup>16-19</sup> The Si  $2p$  core level for example, is shifted by  $\sim 4.2$  eV between Si and  $SiO_2$ , while the Si  $KLL$  Auger is shifted by  $\sim 8.1$  eV.<sup>16</sup> Using specific Auger emission as a probe, partial absorption yield spectra for mixed valence states can be collected. Figure 3 shows the TEY and TFY spectra for oxidized Al. Sampling depths for each mode are different due to the different escape depths of electrons (50 Å) versus x rays (1000 Å). The ratio of the features at 1546 and 1552 eV between the two spectra are different since the

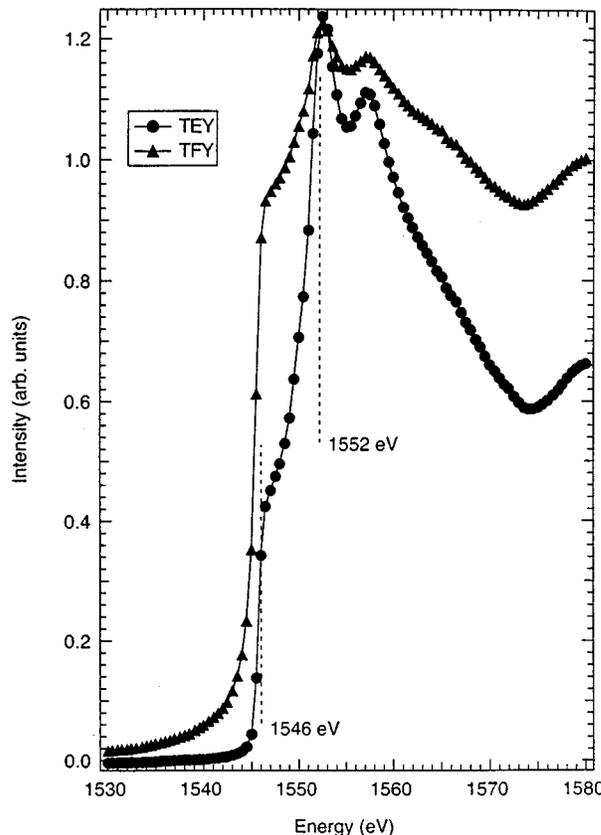


FIG. 3. Al  $K$  edge for oxidized Al collected in TEY and TFY modes.

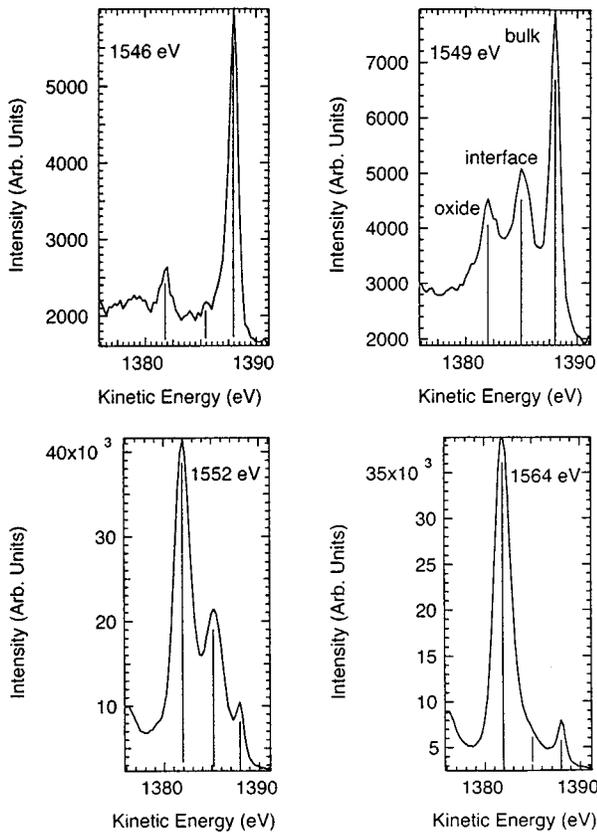


Fig. 4. Comparison of Al *KLL* Auger spectra taken at various excitation energies across the Al *K* edge for oxidized Al.

sampling depth of each experimental mode is different. This system may be used to show the ability of resonant Auger spectroscopy to differentiate between different chemical states and extract partial absorption yields for each state.

Figure 4 shows Auger spectra for oxidized Al at four incident photon energies spanning the Al *K* edge. Three distinct Auger peaks are clearly observed, and each modulates in intensity differently across the edge. We believe that the different modulations indicate the presence of different chemical states within the oxidized Al. There are three different chemical states of the Al:Al bulk metal,  $E_k = 1388$  eV,<sup>20</sup> surface oxide  $\text{Al}_2\text{O}_3$ ,  $E_k = 1382$  eV,<sup>20</sup> and an interface region in between the oxide and the metal in which the oxidation is only partially complete,  $E_k = 1385$  eV.<sup>21–23</sup> Using an Auger spectrum (not shown) well above the edge, these three peaks were fitted using Lorentzians allowing thicknesses of 25, 2, and 4 Å for the surface oxide, metal–oxide interface, and bulk metal, respectively, to be estimated.<sup>24</sup> The escape depth of the Auger electrons in this experiment are such that only a small portion of the nonoxidized bulk of the sample can be observed. The interface between metal and oxide has been observed previously,<sup>21–23</sup> however, measurements were performed on extremely thin oxide layers (1–2 monolayers) grown under carefully controlled conditions using highly surface sensitive photoelectrons of a few tens of electron volts in kinetic energy and absorption measurements

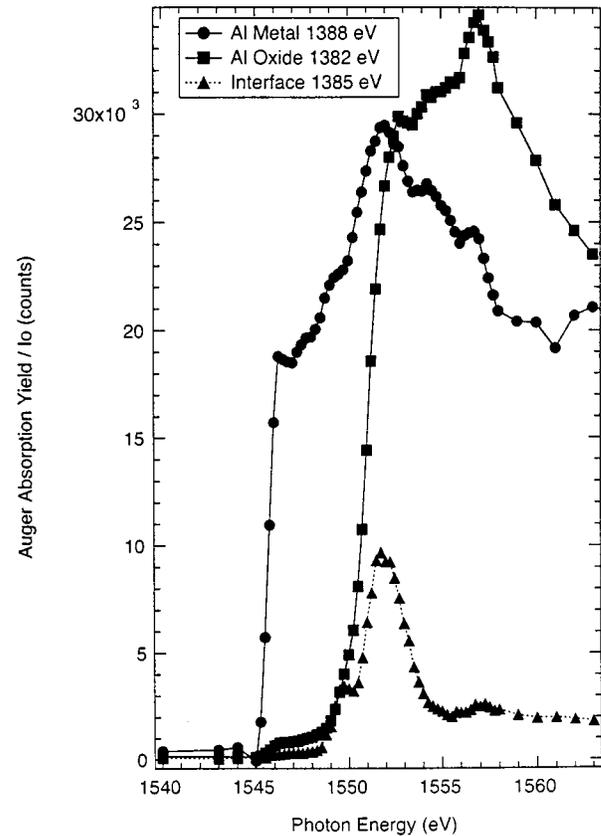


Fig. 5. Partial Auger yields for three valence states of oxidized Al.

at the Al *2p* level. Resonant Auger measurements using *KLL* emission of  $\sim 1385$  eV provides a way of probing interfaces buried under thick oxide layers due to the comparatively large escape depths of the electrons at these energies.

Figure 5 shows the results of collecting partial absorption yields, for each of these three chemical states, across the Al *K* edge. Each spectrum is a result of the different chemical states probed. The contribution of the metal/oxide interface to the absorption spectrum of the sample is small but measurable using Auger emission. Its presence is not measurable from the TEY and TFY, shown in Fig. 3. The TEY/TFY signal from the interface layer is buried under the signals from the two other chemical states. The interface region contributes at most only a few percent to the total yield spectrum as surface sensitive TEY samples a depth of  $\sim 50$  Å.<sup>25</sup>

Ideally the sum of these partial yield spectra should reproduce the total yield measured from the sample. Figure 6 compares the TEY spectrum and the sum of the partial yields extracted from the resonant Auger spectra. The partial yield of the nonoxidized Al layer were scaled prior to addition to reflect the different depth sensitivities of TEY and Auger measurements.<sup>24</sup> In the Auger spectra, the bulk Al metal contributed only  $\sim 10\%$  to the entire signal, whereas in TEY the metal contributes  $\sim 50\%$  to the signal based upon the escape depths of the detected electrons for each technique.<sup>24</sup> Both spectra agree quite well both in terms of intensity and in the shape of the near-edge features.

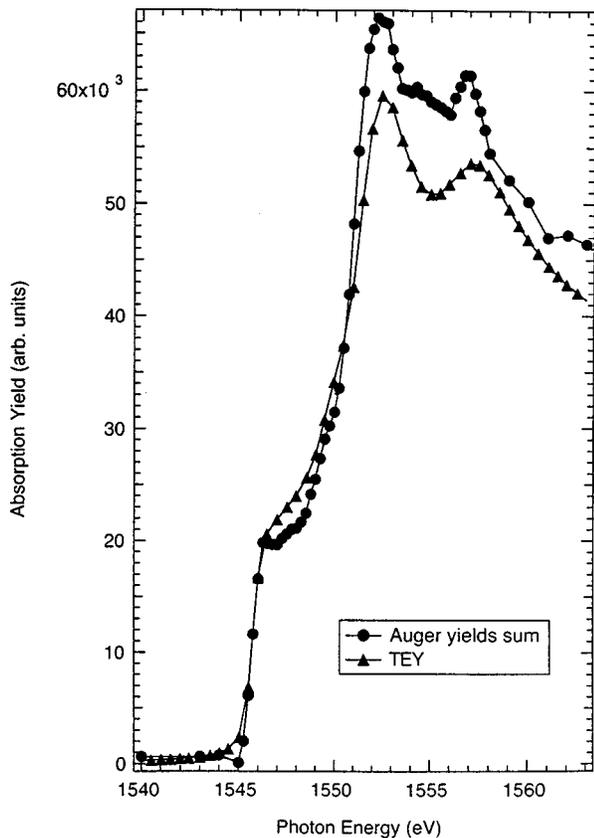


FIG. 6. Comparison of TEY to the sum of partial yields generated from resonant Auger spectra for oxidized Al.

#### IV. CONCLUSIONS

Resonant Auger experiments on a variety of metallic systems were studied. Partial absorption yields were measured for oxidized Al and three chemical states were resolved showing that resonant Auger emission may be used to resolve chemical and electronic features in mixed valence materials.

#### ACKNOWLEDGMENTS

Work at Argonne is supported by the U.S. Department of Energy, Basic Energy Sciences, under Contract No. W-31-

109-Eng-38. Work at the University of Western Ontario was supported by a grant from the National Sciences and Engineering Research Council of Canada. Anton Stampfl was supported by the Australian Synchrotron Research Program which is funded by the Commonwealth of Australia under the Major National Research Facilities Program.

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<sup>25</sup>Estimated from the universal electron escape depth curve assuming that the primary source of TEY signal is from secondary electrons of a few electron volts in kinetic energy.